A Core/Shell Nanoparticle Approach for Photoreversible Fluorescence Modulation of Hydrophobic Dye in Aqueous Media

Jian Chen, Fang Zeng, Shuizu Wu,* Qiming Chen, Zheng Tong

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China
Supporting Information

1. Characterizations:

Figure S1. $^1$H NMR spectrum of SPCOOH. $^1$H NMR (400 MHz, deuterated DMSO, 25$^\circ$C, TMS) (ppm): 1.0 – 1.3 (2 $CH_3$), 2.6 ($CH_2$COO), 3.4 – 3.5 ($CH_2$N), 5.9 – 6.0 (olefinic protons, 2H), 6.6 – 8.2 (aromatic protons), 12.0 (COOH, hydrogen bonding).
Figure S2. $^1$H NMR spectrum of spiropyran-linked methacrylate (SPMA) monomer.

$^1$H NMR (400 MHz, CDCl$_3$, 25°C, TMS) (ppm): 1.0 – 1.3 ($CH_3$ of spiropyran, 6H), 1.8 – 1.9 ($CH_3$ of HEMA, connected to olefinic carbon, 3H), 2.6 – 2.7 ($CH_2$COO of spiropyran, 2H), 3.5 – 3.6 ($CH_2$N of spiropyran, 2H), 4.2 ($CH_2$O of HEMA, 4H), 5.5 -6.0 (olefinic protons, $CH_2$ and two $CH$, 4H), 6.6 – 8.1 (aromatic protons).
Figure S3. Excitation spectrum for NBD/nanoparticle complex in water ($\lambda_{em} = 530$nm).
2. Change in appearance of NBD/nanoparticle dispersion upon UV or visible light irradiation

Figure S4. Photograph for the NBD/spiropyran-containing nanoparticle complex in water after visible light irradiation (a) and UV irradiation (b). The appearance of (a) is the combined effect of absorption of NBD, emission of NBD (excited by the environmental light) as well as the absorption of spiropyran (in SP state); and the appearance of (b) is the combined effect of the absorption of NBD as well as the adsorption and emission of spiropyran (in MeH state).
3. Calculation of Förster radii \( (R_0) \) \(^{\text{[1,3,4]}}\) and some other parameters

**Determination of fluorescence quantum yield of the donor NBD**

The quantum yield can be described as follows:

\[
\Phi_D = \Phi_S \times \frac{F_D}{F_S} \times \frac{A_S}{A_D} \times \left(\frac{n_D}{n_S}\right)^2
\]

Where \( \Phi_s \) is the fluorescence quantum yield of the standard (rhodamine B in ethanol, 0.65, 25°C) \(^{[2]}\), \( F_D \) and \( F_S \) are the integral area of fluorescence intensity of the donor and the standard at the same excitation wavelength, respectively; \( A_D \) and \( A_S \) are the absorbance of the donor and the standard at the defined excitation wavelength, respectively; \( n_S \) and \( n_D \) are the refractive index at 25°C of the solvent of standard (ethanol) and the matrix of donor (PMMA), respectively.

![Absorption spectrum](image)

Figure S5. Absorption spectrum for dispersion of spiropyran-free nanoparticles and dispersion of NBD/ spiropyran-free nanoparticles.

To determine the quantum yield of NBD in nanoparticle system, we first need to measure the
actual absorbance of NBD (at 490 nm) in nanoparticle system. Since the NBD/nanoparticle complex dispersion exhibits relatively strong light scattering effect (as shown in Figure S5), to eliminate the error caused by light scattering effect, we also measured the absorption spectrum for the neat nanoparticles (with neither NBD nor spiropyran), and the actual absorbance value for NBD at 490nm can be obtained by the deduction of the absorbance of neat nanoparticle dispersion at 490nm from the apparent absorbance value of NBD/neat nanoparticle dispersion.

The $\Phi_D$ of NBD in nanoparticle system was calculated to be 0.68.

**Calculation of the Förster radii ($R_0$) [1, 3, 4] and determination of experimental energy transfer efficiency**

The Förster’s distance or critical distance $R_0$ is the characteristic distance, at which the efficiency of energy transfer is 50%. The magnitude of $R_0$ is dependent on the spectral properties of the donor and the acceptor molecules. If the wavelength $\lambda$ is expressed in nanometers, then $J(\lambda)$ is in units of M$^{-1}$cm$^{-1}$nm$^4$ and the Forster distance, $R_0$ in angstroms (Å), is expressed as follows [Eq. (1)]:

$$R_0 = 0.2108 \times \left[ \kappa^2 \times \Phi_D \times n^{-4} \times J(\lambda) \right]^{1/6} \quad [\text{Eq. (1)}]$$

$\kappa^2$ is the orientation factor for the emission and absorption dipoles and its value depends on their relative orientation, $n$ is the refractive index of the medium and $\Phi_D$ is the quantum yield of the donor. $J(\lambda)$ is the overlap integral of the fluorescence emission spectrum of the donor and the absorption spectrum of the acceptor (Figure S6) [Eq. (2)].

$$J(\lambda) = \int_0^\infty F_D(\lambda) \times \varepsilon_A(\lambda) \times \lambda^4 \times d\lambda \quad [\text{Eq. (2)}]$$

$F_D(\lambda)$ is the fluorescence intensity of the donor in the absence of acceptor normalized so that $\int_0^\infty F_D(\lambda)d\lambda = 1$; $\varepsilon_A(\lambda)$ is molar extinction coefficient of the acceptor, $\lambda$ is wavelength. In current
experimental conditions, for sample NP-A1, the $J(\lambda)$ was calculated to be $7.62 \times 10^{14} \text{M}^{-1}\text{cm}^{-1}\text{nm}^{4}$. The Förster distance ($R_0$) has been calculated assuming random orientation of the donor and acceptor molecules taking $K^2 = 2/3$, $n = 1.49$ (PMMA), and $\Phi_D = 0.68$.

For NBD (donor) and McH form of spiropyran (acceptor) in current experimental situation, by using a commercial software Origin 7.0 as the integral tool, we calculated $R_0 = 43\text{Å}, 42\text{Å}$ and $42\text{Å}$ for sample NP-A1, NP-A3 and NP-A4. Energy transfer will be effective within the range $R_0 \pm 50\%$ $R_0^{[5]}$.

**Figure S6.** Fluorescence spectrum of NBD in nanoparticle system (donor), and absorption spectrum of spiropyran-containing nanoparticles (acceptor, sample NP-A1) in water (with the light scattering effect eliminated).

Experimental energy transfer efficiencies ($E$) given in Table 2 (main text) were calculated from $E = 1-I/I_0$, where $I_0$ is the fluorescence intensity of NBD/spiropyran-containing nanoparticle complex upon visible light irradiation; $I$ is that upon UV irradiation.
Calculation of the average distance between spiropyran moieties

Assuming that the distribution of spiropyran moieties in the whole nanoparticle core is homogeneous, a sphere occupied by a spiropyran molecule can be defined by its diameter $D_{SP}$, which corresponds to the distance between two spiropyran moieties. As the volume occupied by the spiropyran molecules contained in polymer matrix is the volume of one nanoparticle, one can write [1],

$$D_{SP} = 2 \left( \frac{3 \times V_{NP}}{4\pi \times N_{SP/NP}} \right)^{1/3}$$

where $V_{NP}$ is the particle’s volume and $N_{SP/NP}$ is the number of spiropyran moieties per nanoparticle.

This calculation assumes all monomers are polymerized and the density of PMMA core is 1.19 g/cm$^3$. The calculated values are given in Table 2 (main text).

References


4. Fluorescence intensities recorded upon UV and visible light irradiation for repeated cycles.

Table S1. List of fluorescence intensities for NBD/nanoparticle complex (NBD concentration: 1.07×10^{-5} M, \( \lambda_{\text{ex}} = 490\text{nm} \)) recorded at 533 nm upon UV illumination and visible light irradiation cycles.

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<th>Intensity (a.u.)</th>
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<th>Upon Vis.</th>
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